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## **Millimeter- and Submillimeter-wave Nanoscience: LDRD Project 122359 Final Report**

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### **Abstract**

LDRD Project 122359 was a nine-month, late-start effort that pursued initial experiments studying the fundamental electrodynamic response properties of various nanomaterials from millimeter-wave (above roughly 30 GHz) up to submillimeter-wave (above roughly 0.1 THz) frequencies. The nine months of this project's duration produced two main empirical findings. First, Fourier transform reflectance spectroscopy on SrTiO<sub>3</sub> nanocrystals from 0.2 to 10 THz frequency showed signatures of two optical phonons that correspond to known optical modes in bulk crystal SrTiO<sub>3</sub>. However, quantitative differences between the nanoparticle and bulk spectra suggest that one or both of these phonons may shift frequency and weaken in nanoparticles relative to bulk crystal. Second, heavily doped *n*-type GaAs nanowires were synthesized for the purpose of creating high frequency diodes to study non-linear frequency conversion properties of compound semiconductor nanowires. It was found that incorporation of a heavy concentration of dopants interferes with the growth of these nanowires. While DC measurements showed reasonable diode-like current-voltage properties, the current state-of-the-art material properties of these nanowires are still unsuitable for millimeter-wave testing and applications.



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## 1. Introduction

The research done under this late-start LDRD was to characterize possibly unique and interesting electrodynamic properties of nanomaterials at millimeter-wave and submillimeter-wave frequencies, roughly several tens of GHz up to about 10 THz. In particular, the aim was to discover whether the fundamental electrodynamic response characteristics (*e.g.*, reflectance, AC conductance, and non-linearity) of some nanomaterials could be qualitatively different from the well-established conventional response in macroscopic or bulk crystals of the same material, owing solely to the physics of having nanometer-scale dimensions.

Over the course of this nine-month project we have worked with strontium titanate ( $\text{SrTiO}_3$ ) nanocrystals, which offer a direct comparison with bulk single-crystal  $\text{SrTiO}_3$ , and with heavily doped *n*-type GaAs nanowires.  $\text{SrTiO}_3$  is a physically very interesting material by virtue of its being a “incipient” ferroelectric. [1] The bulk crystal has two well-known transverse optical phonons that are “soft”, *i.e.* below 10 THz in frequency, which control the material reflectance at millimeter- and submillimeter-wave frequencies. There is great interest in GaAs nanowires as the basis material for non-linear millimeter- and submillimeter-wave devices, owing to the high mobility of electrons that can be achieved in bulk GaAs and the intrinsically small geometrical capacitances that can be achieved straightforwardly using nanowires. Unfortunately, it has proven very difficult to synthesize GaAs nanowires with sufficiently high dopant concentrations (*i.e.*, small electrical resistance) to be useful at high frequencies.

## 2. Submillimeter-wave Reflectance of $\text{SrTiO}_3$ Nanocrystals

$\text{SrTiO}_3$  is a very interesting material from a ferroelectric and phase transition standpoint because it seems like it should undergo a ferroelectric phase transition at around 40 K, but it doesn't. [1] The “incipient” ferroelectric nature is controlled by two optically-active transverse optical (TO) phonons at 2.6 THz and 5.3 THz (in bulk at room temperature) that control the electrodynamic reflectance of the material below 10 THz.

Using a Bruker Fourier transform spectrometer (FTS) specifically modified to work at THz frequencies via a mercury lamp broadband THz source, thin Mylar beam splitter, and a liquid helium cooled THz bolometer detector [2], we directly measured the

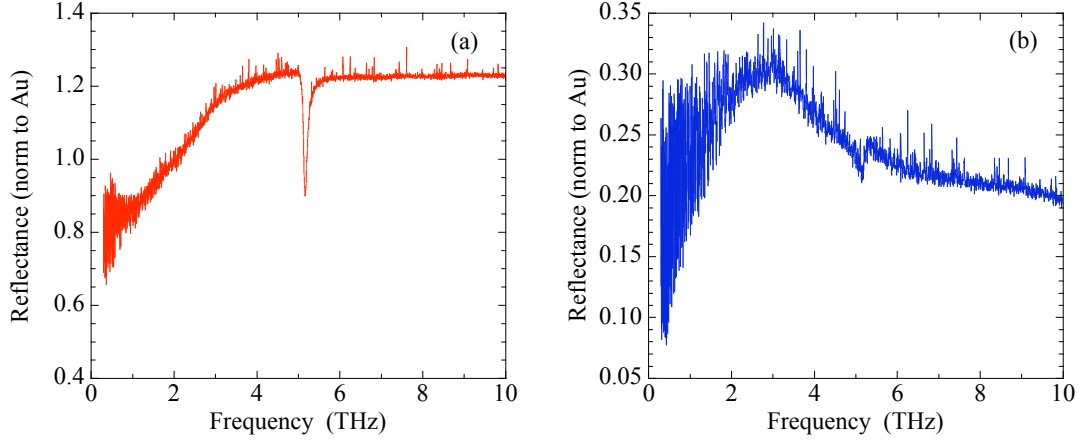


Figure 1: FTS reflectance spectra at 10° incidence of (a) a bulk SrTiO<sub>3</sub> single crystal, and (b) SrTiO<sub>3</sub> nanocrystals embedded in a matrix. Both spectra are normalized to the reflectance of a gold mirror.

reflectance spectra for a pellet composed of SrTiO<sub>3</sub> nanocrystals embedded in a matrix, and for a commercial SrTiO<sub>3</sub> bulk single crystal sample. Resulting reflectance spectra (at 10° incidence angle, normalized to the reflectance of a reference gold mirror) are shown in Fig. 1(a) for the bulk crystal and Fig. 1(b) for the nanocrystal samples up to 10 THz.

The bulk single crystal shows the expected classical reflectance signatures of the two soft TO phonons. [3] A broad rise in reflectance with frequency through roughly 2.6 THz is due to the lowest TO phonon. There is no resonant peak because this phonon is overdamped due to strong anharmonic decay into acoustic phonons. A clear underdamped phonon resonance is apparent at 5.3 THz.

The reflectance spectrum of the SrTiO<sub>3</sub> nanocrystal sample is weaker due to a smaller volume filling fraction of SrTiO<sub>3</sub> material. Nonetheless, it shows similar features but is qualitatively different from the bulk crystal. At low frequencies there is a rise in reflectance with increasing frequency, but this rise tops out at a lower frequency, about 3 THz, compared to the bulk crystal, whose reflectance maximizes around 4 THz. There is then a background of decreasing reflectance in the nanocrystal sample, compared to a flat reflectance in the bulk crystal. An underdamped phonon resonance is apparent in the nanocrystal sample near 5.1 THz, but it is much weaker and broader compared to the much stronger phonon resonance in the bulk crystal at 5.3 THz.

We do not yet fully understand the science behind the qualitative differences in the reflectance spectra between bulk and nanocrystal SrTiO<sub>3</sub> material. The two forms of



material share the same general low frequency phonon structure. However, the nanocrystals show a slight but empirically significant shift to lower phonon frequencies, as well as a general weakening of phonon structure in the reflectance spectrum. We can speculate that the shift may be a result of interactions between surface boundaries with the bulk phonon modes, which are expected to be far more significant in nanocrystals, with their very high surface-to-volume ratios, compared to bulk. The weakening of the phonon structure may suggest a smaller oscillator strength in the coupling of phonons to the high-frequency incident electromagnetic field.

### 3. Doped GaAs Nanowires for Frequency Conversion Diodes

Non-linear devices are extremely useful at high frequencies for frequency up- and down-conversion and rectification of high-frequency AC signals to DC for signal detection. It is therefore of great interest to investigate non-linear electrodynamic properties of materials and device structures. For microwave through low millimeter wave work, diodes made from heavily doped *n*-type and *p*-type bulk compound III-V semiconductor crystals are favored owing to the very high electron mobility, and hence very fast response time, possible in III-V semiconductors like GaAs. However, it becomes difficult to build such diodes to operate at frequencies above roughly 100 GHz owing to parasitic resistance ( $R$ ) and capacitance ( $C$ ), which introduce a characteristic time constant  $RC$ . Frequencies higher than  $1/2\pi RC$  get shunted around the non-linear device rather than go through it, so  $1/2\pi RC$  sets a practical limit on the highest frequency for which a non-linear device is useful. The aim therefore is to reduce  $RC$  to as small a time as possible for work at millimeter- and submillimeter-wave frequencies. Using bulk GaAs material where heavy doping can make  $R$  quite small, this problem reduces to achieving very small parasitic capacitance. Typically, this is done by using very expensive, complicated, and slow electron beam fabrication methods to make very small diode ( $\sim 250$  nm diameter) contact dimensions, [4] which reduces the parasitic geometrical capacitance enough so that  $1/2\pi RC$  can significantly exceed 1 THz.

Because nanowires have intrinsic diameters ranging from 50 to 200 nm, it is hoped that using the nanowire form of a III-V semiconductor such as GaAs could make a non-linear diode with intrinsically small geometrical parasitic capacitance  $C$  without the need

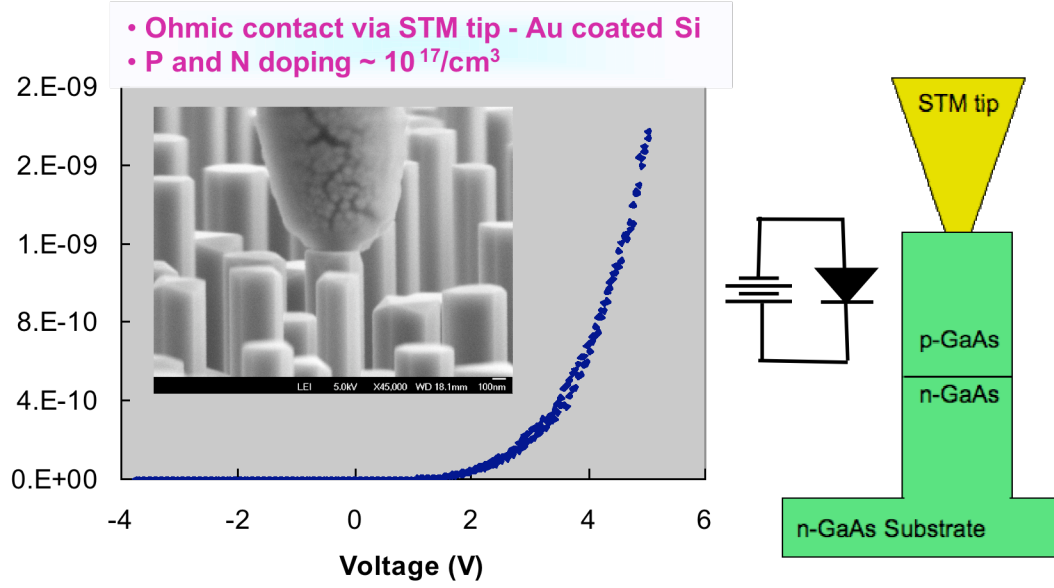


Figure 2: (left) Scanning electron micrograph image of a conducting scanning probe tip contacting the diameter face of *pn* junction GaAs nanowire, with the highly non-linear diode-like current-voltage characteristics of the nanowire device. (right) Cartoon representation of the equivalent circuit and physical layout of the measurement.

for expensive and complicated electron beam lithography methods. To accomplish this requires growing GaAs nanowires with sufficiently heavy *n*-type and *p*-type doping concentration to reduce the nanowire resistance  $R$  so that the  $RC$  time constant can be pushed down to picoseconds, corresponding to at least hundreds of GHz maximum frequency. While high quality undoped GaAs nanowires are grown by many groups, it has proven difficult to dope such nanowires to a level that produces resistivities as low as is possible in bulk GaAs crystals.

Under this project in collaboration with Prof. Diana Huffaker's group at UCLA, we have attempted to grow GaAs nanowires with high enough doping concentration to be useful as low parasitic  $RC$  high-frequency diodes. Using a mask-defined, catalyst-free epitaxial growth technique, highly faceted, extremely vertical GaAs nanowires with diameters of 50 to 300 nm were grown with doping levels estimated to be about  $5 \times 10^{17} \text{ cm}^{-3}$  bulk equivalent, both *n*- and *p*-type, which corresponds to near-degenerate dopant concentrations in bulk crystals. In addition, this growth method could be used to make abrupt internal pn junctions in single nanowires (see Fig. 2(right)), thereby incorporating and internal non-linear diode interface.

Fig. 2(left) shows a scanning electron micrograph image of one of these nanowires being electrically contacted by a conducting scanning probe tip. It was found that trying to incorporate a high concentration of dopants caused the nanowire growth to produce far less uniformity in nanowire diameters and lengths compared to undoped nanowire growth for reasons that are not understood. Incorporating a high concentration of dopant materials somehow interferes with the growth of the nanowires. Fig. 2(b) shows some DC current-voltage characteristics of a few such nanowires taken using the scanning probe tip. Many, though not all, of these nanowires show reasonable DC diode characteristics, which is promising for high-frequency non-linear response measurements.

While the geometric capacitance of these nanowires, contacted on the end (diameter) faces is estimated to be quite small (of order fF), unfortunately the very high variability of these nanowires in terms of size, aspect ratio, resistivity, and uniformity electrical properties down the length of any individual nanowire make them unsuitable for integration into our millimeter-wave test platforms for high-frequency testing. The also parasitic resistances  $R$  in these nanowires are also high enough to make the maximum frequency  $1/2\pi RC$  drop well below 100 MHz. Apart from the problem of high dopant levels interfering with the nanowire growth process, the incorporated dopants apparently produce a significantly higher resistivity in nanowires compared to bulk crystals of the same material at same nominal equivalent dopant concentrations. Indeed, this observation has been reported for silicon nanowires. [5] Speculations about why this may be so include a reduction in activated dopants owing to more interstitial dopant atoms incorporated in the nanowire growth process, and much higher scattering of electrons from surface roughness and surface states in nanowires compared to bulk crystals. Some preliminary efforts at surface passivation of the nanowires to reduce surface states have been attempted, with uncertain success at this time. Nevertheless, this research finding points out a major difficulty that must be overcome in the practical use of nanomaterials in any high-frequency device application.

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